

GENERAL MOTORS CORPORATION

TECHNICAL REPORT ON

CARBON DIOXIDE DISSOCIATION RATES
BEHIND SHOCK WAVES

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Moffett Field, California

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M. Steinberg

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FOREWORD

This report presents the results of an experimental study conducted at GM Defense Research Laboratories, during the period March 1963 to March 1964, on the dissociation of carbon dioxide at elevated temperatures behind shock waves. This work was performed for the Ames Research Center, National Aeronautics and Space Administration, under Contract No. NAS 7-217. A previous report (GM DRL Technical Report No. TR64-14, February 1964) covers the analytical phase of this contract.

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ABSTRACT

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The dissociation rates of carbon dioxide have been measured at elevated temperatures behind shock waves in mixtures with argon and nitrogen. The disappearance of carbon dioxide was monitored by following the emission in the 4.3μ and 2.7μ infrared bands. Over the range from 3,300 to 6,000°K at total pressures of 0.5 to 1.0 atm, the bimolecular rate constant for the process



in mixtures of 0.5 to 2.0 percent carbon dioxide in argon is given by

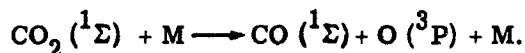
$$k_A = 2.26 \times 10^{11} T^{1/2} e^{-71,900/RT} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}$$

For dilute mixtures of 1.0 percent carbon dioxide in nitrogen at shock temperatures from 3,100 to 7,700°K the corresponding rate constant is

$$k_{N_2} = 1.18 \times 10^{11} T^{1/2} e^{-73,200/RT} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}.$$

The rate constant in nitrogen mixtures was independent of the total pressure from 0.5 to 5.0 atm for a series of tests at about 4,800°K. Variations of mixture ratios of up to 20 percent carbon dioxide in nitrogen yielded results within the experimental spread for the dilute mixtures.

The observed activation energies are well below the dissociation energy (126 kcal/mol) for the process



Possible mechanisms for the dissociation are discussed in the report.

Author

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INTRODUCTION

Consideration of the problems attendant on the entry of ballistic probes into the atmospheres of Mars and Venus points up the need for kinetic studies on the high-temperature carbon dioxide-nitrogen system. The radiative contribution of CN formed in the stagnation zone on a Martian probe could significantly increase the stagnation heating.^{(1)*} At the higher velocities of a Venus entry, radiative heating could be even more important. Similarly the ionization produced in the flow field about such probes is dependent on the complex chemistry leading to the ionized species. The primary process in the high-temperature carbon dioxide-nitrogen system from which all subsequent chemistry follows is the dissociation of carbon dioxide. Howe, Viegas, and Sheaffer⁽²⁾ in an analysis of the nonequilibrium dissociation flow field behind shocks in carbon dioxide pointed up the need for rate information for carbon dioxide dissociation. The current report describes some measurements on the dissociation rates behind shocks in CO₂-Ar and CO₂-N₂ mixtures.

Until recently, little information indeed was available on carbon dioxide dissociation kinetics. Hurle and Gaydon⁽³⁾ reported a few measurements on dissociation relaxation behind shock waves in pure carbon dioxide. Brabbs, Belles and Zlatarich⁽⁴⁾ made measurements on carbon dioxide-argon mixtures over the range from 2,500 to 3,000°K. Davies⁽⁵⁾ reported on measurements on carbon dioxide mixtures in argon and nitrogen at 3,500 to 6,000°K and more recently⁽⁶⁾ to 11,000°K in argon mixtures.

Previously reported rate measurements⁽⁷⁾ on carbon dioxide-argon mixtures are summarized in the present report, along with new results on carbon dioxide-nitrogen mixtures. Carbon dioxide disappearance was followed by recording the

* Raised numbers in parentheses indicate references, listed at the end of this report.

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variation in emission in the 2.7μ or 4.3μ bands. Dilute mixtures of carbon dioxide in argon and nitrogen were used to study the dissociation under conditions of near-constant temperature and pressure. In addition, mixtures of up to 20 percent carbon dioxide in nitrogen were studied. The carbon dioxide-argon studies were conducted in a six-inch-diameter shock tube behind incident shocks. The nitrogen diluent studies were performed in a three-inch-diameter shock tube behind reflected shocks which were required to produce the temperatures necessary for the dissociation. The shock tubes and associated instrumentation are discussed in the next section.

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EXPERIMENTAL APPARATUS

SHOCK TUBES

Both shock tubes used in the study are simple uniform bore tubes. The 6-inch tube has a 4-foot driver and a 30-foot test section. The tube has a honed bore to facilitate cleaning and pump down. Stainless steel scribed diaphragms are used in a small double diaphragm rupture assembly designed to reproducibly rupture diaphragms at predetermined pressures. A short section three inches long with a diaphragm on each end is clamped between the driver and test sections. In operation, the test gas is admitted to the test section to pressure p_1 . The helium driver gas is then admitted to the driver and intermediate sections to a pressure $0.5 p_4$, where p_4 is the desired driver pressure. The valve to the intermediate section is then closed and helium is pumped into the driver section to the pressure p_4 . The diaphragms are chosen to rupture at about $0.75 p_4$, thus they readily withstand the differential, $0.5 p_4$, across each diaphragm. To fire the tube the short section is vented to the atmosphere, increasing the differential across the upstream diaphragm. The upstream diaphragm then ruptures, followed by the downstream diaphragm.

The driver and test sections are evacuated by a mechanical pump. In addition, the test section is evacuated by a 4-inch VEECO oil diffusion pump. The large vacuum port at the shock tube is located near the diaphragm and closes flush with the tube wall to avoid generating disturbances behind the incident shocks. Initial pressures in the test section are measured with Wallace and Tiernan absolute pressure gauges. Commercial helium is used as the driver gas. Driver pressures of up to 2,000 psi are available and are measured with Heise bourdon-tube gauges.

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The 3-inch shock tube has a 4-foot driver and 24-foot test section and is in all other respects very similar to the 6-inch tube. Both shock tubes have identical gas handling systems. Matheson gases (argon-purity 99.998 percent; nitrogen-prepurified grade-purity 99.996 percent; and carbon dioxide-Coleman grade-purity 99.99 percent) were used to prepare mixtures by the method of partial pressures in 16-liter stainless steel gas storage bottles.

The shock tubes are cleaned before each firing by drawing snug-fitting cylindrical plugs wrapped with alcohol-soaked cheese cloth through the test section. The process is repeated several times with clean cloth until the plugs come through clean.

SHOCK VELOCITY

The conditions behind incident and/or reflected shocks in the carbon dioxide mixtures in argon or nitrogen are determined from measurements of the shock velocities. Shock velocities are measured by monitoring the transit time across two measured intervals along the test section. Thin film gauges, prepared from Hanovia Bright Platinum No. 5 painted and fired on glass blanks between hermetically sealed feed-through electrical leads, are used to sense shock arrival at the velocity stations.⁽⁸⁾ The gauges are mounted flush with the shock-tube wall. The outputs of the gauges are amplified and used to start and stop a pair of microsecond time interval meters. Shock velocities can be measured to about 1/2 percent, corresponding to less than 1 percent uncertainty in equilibrium temperatures behind incident or reflected shocks. Depending upon the validity of the assumptions regarding departures from equilibrium, the uncertainties in the temperature assessments may, of course, exceed 1 percent.

OPTICAL SYSTEM

The same optical system was used for the argon and nitrogen diluent studies in the 3-inch and 6-inch tubes, respectively. Carbon dioxide disappearance is followed by monitoring the 4.30μ or 2.85μ emission behind the shocks.

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A schematic of the optical system is shown in Figure 1. Pairs of calcium fluoride windows, W (0.50 in. dia. in the 6-inch tube and 0.375 in dia. in the 3-inch tube), are mounted almost flush with the shock tube walls, T. A pair of slits, S_1 and S_2 , 1 mm wide and made of 3 mil shim stock are lined up perpendicular to the tube axis. The slits along with the globar source, G, and the sector wheel, C, serve to align the optical system and check its response before each firing.

Radiation from the shocked gases is collimated by S_2 and S_3 , which is also 1 mm wide. The fields of view parallel to the tube axes are a maximum of 2 mm. S_2 is imaged on the entrance slits of a Perkin Elmer Model 98 Monochromator, P, via mirrors M_1 , M_2 , and M_3 . The exit slit of the monochromator is imaged with a 6-fold demagnification by an ellipsoidal mirror, M_4 , on the sensitive element of a Philco ISC-301 indium antimonide detector. The detector output is fed into a Tektronix Type 1121 wideband amplifier across a 500-ohm load resistance to maintain the fast-rise-time capability of the system. The output of the 1121 amplifier goes to a Tektronix oscilloscope and the trace is recorded with a polaroid camera. The detector-amplifier combination rise time was determined by sweeping a focused light beam across the sensitive element of the detector. A high speed Beckman and Whitley Q spoiler was used to produce a pulsed beam having a rise time of $0.4\mu\text{sec}$. The detector-amplifier system tracked the rising signal. However, the decay time was found to be about $1\mu\text{sec}$. The response times are adequate for the present study.

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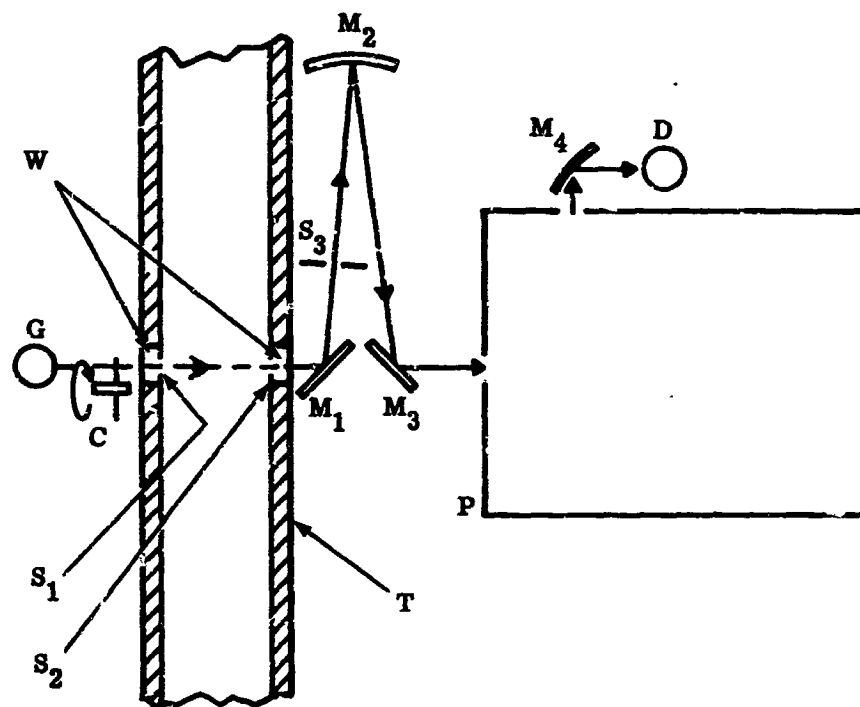


Figure 1 Shock Tube Optics

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RESULTS

CARBON DIOXIDE-ARGON MIXTURES

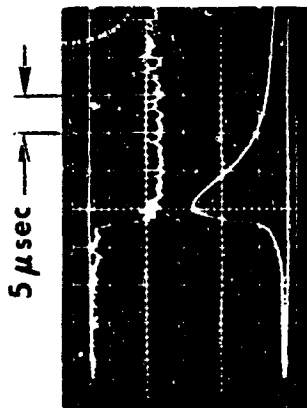
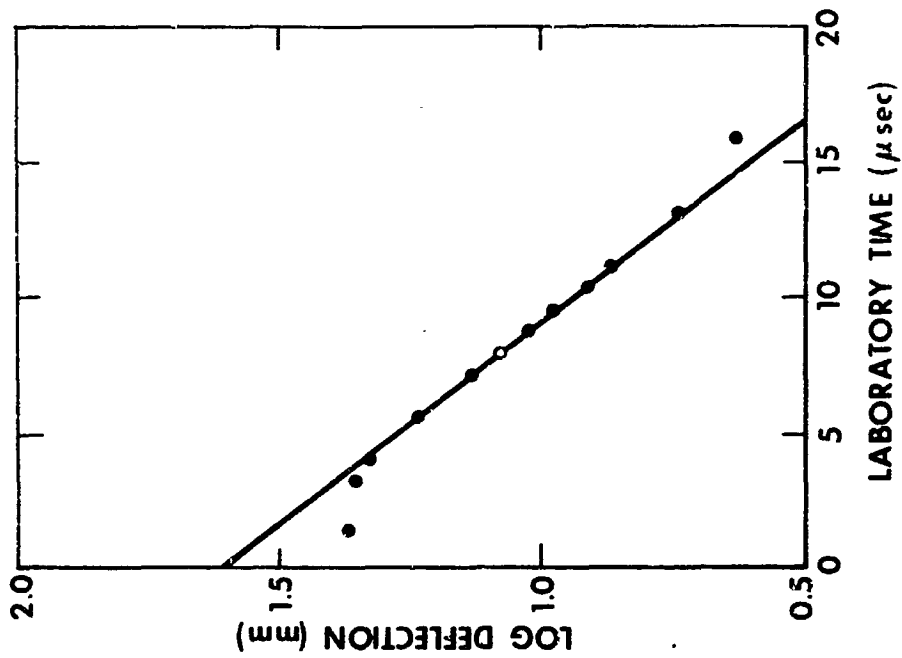
The dissociation of carbon dioxide in argon mixtures was monitored at 4.30μ . Observations were made behind incident shocks at a station 4 feet from the end wall of the 6-inch shock tube. In order to avoid excessive attenuation of the emitted radiation by atmospheric carbon dioxide in the long optical path outside the shock tube, the optical system was enclosed in a polyethylene bag and flushed with nitrogen.

Carbon dioxide decay measurements were made in mixtures of 0.5, 1.0, and 2.0 percent carbon dioxide in argon at temperatures from 3,300 to 6,000°K at pressures from 0.5 to 1.0 atm. Below 3,300°K the reaction was too slow to get measurable decays in the available test time.

A typical oscilloscope trace is shown in Figure 2. The upper trace is the output of an 1P28 photomultiplier located in the same plane as the IR system. The photomultiplier was only used to accurately mark the shock arrival at the test station. The output from a thin film gauge located a few inches ahead of the observation station triggered the oscilloscope sweep. The IR signal shows a slow rise time of about $2\mu\text{sec}$ at 5,000°K in Figure 2. The slow rise is probably due to the transit time of the shock across the field of view coupled with the vibrational relaxation of carbon dioxide. The shock temperature calculations were based on vibrational equilibrium of the carbon dioxide. The IR peak is then followed by a decay as the carbon dioxide dissociates.

A plot of the logarithm of the output signal against time is shown on the graph in Figure 2. The slow rise of the signal is again apparent followed by a well-defined exponential decay. At long times the emission approaches a plateau, probably due to (1) the approach to equilibrium and the onset of back reaction and (2) the production of carbon monoxide which emits in this spectral region providing a

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OSCILLOSCOPE RECORD

UPPER TRACE -
PHOTOMULTIPLIER OUTPUT

LOWER TRACE -
IR (4.30 μ) OUTPUT

0.5% CO₂ IN ARGON

P₁ = 10mm H₂

U_s = 2.30 mm/μsec

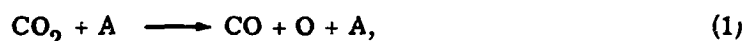
T₂ = 5000° K

Figure 2 Typical Data Record

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background intensity. The existence of the background level is more noticeable as the monitor wavelength is increased toward the carbon monoxide vibrational fundamental at 4.67μ . It was to minimize this complication that the measurements were made at 4.30μ , which necessitated the use of the polyethylene bag and nitrogen flush system. Sulzmann⁽⁹⁾ has shown that the absorption of carbon dioxide in carbon dioxide-argon mixtures at 4.25μ follows the Lambert-Beer's Law at temperatures in excess of $3,200^\circ\text{K}$ for the optical densities encountered in the present study. In the dilute mixtures used here the 4.30μ emission is then proportional to the carbon dioxide concentration, and the exponential decay of the signal in Figure 2 indicates a first-order decay in the carbon dioxide concentration.

Assuming the overall reaction to be



$$-\frac{d(\text{CO}_2)}{dt} = k_A (\text{CO}_2) (\text{A}) \quad (2)$$

and $(\text{CO}_2) = (\text{CO}_2)_0 e^{-k_A (\text{A}) t} \quad (3)$

where (i) = molar concentration of i^{th} constituent (mol/cm^3)
 (i)₀ = concentration immediately behind the shock
 k_A = overall rate constant.

The slope of a plot of $\ln(\text{CO}_2)$ against time behind the shock gives the overall rate constant,

$$k_A = -\frac{1}{(\text{A})} \frac{d \ln(\text{CO}_2)}{dt} \quad (4)$$

Similarly, the slope of the plot of $\log(\text{intensity})$ against time (Figure 2) yields k_A .

A plot of the $\log(k/T^{1/2})$ against $1/T$ is shown in Figure 3. It can be seen from the plot that although the initial $(\text{CO}_2)/(\text{A})$ ratios were varied by a factor of four, the rate constants show approximately a factor of two spread with no systematic dependency on $(\text{CO}_2)/(\text{A})$. Thus, the form of Equation (2) appears consistent with the data.

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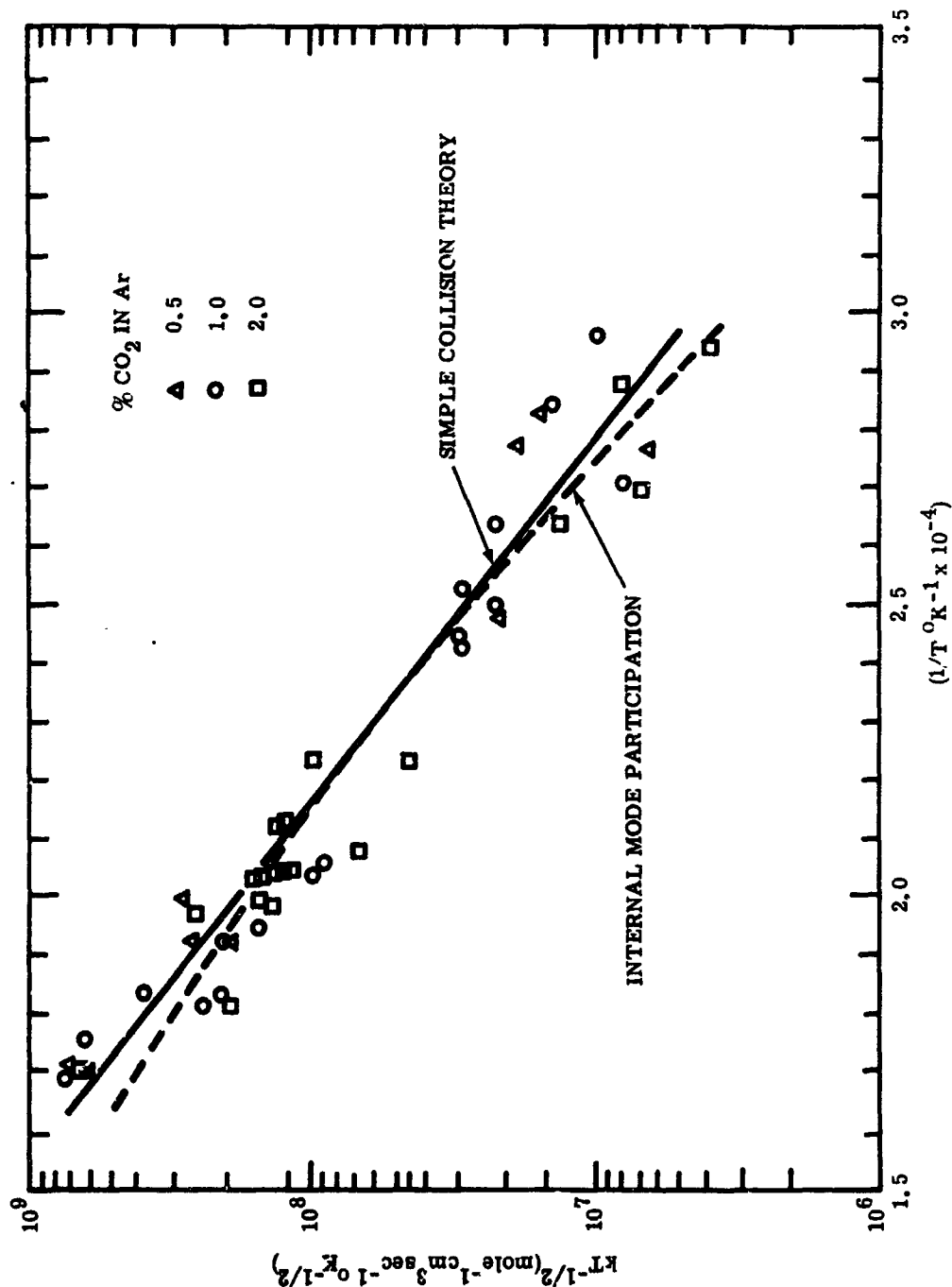


Figure 3 Bimolecular Rate Constants for Carbon Dioxide Dissociation in Argon

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A least-square fit of the Arrhenius equation to the data is shown by the solid line in Figure 3 and yields

$$k_A = 2.26 \times 10^{11} T^{1/2} e^{-71,900/RT} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}. \quad (5)$$

The probable error in the pre-exponential term is 23 percent. The probable error in the activation energy is 1,900 cal/mol. The collision efficiency is 0.02, a reasonable value. Molecular diameters of 4.59 Å for carbon dioxide and 3.64 Å for argon, obtained from viscosity measurements, were used to calculate the efficiency.

The apparent activation energy of 72 kcal/mol is far below the dissociation energy of about 126 kcal/mol (at temperatures of this study) that would be required for the simple collision model in which only the kinetic energy along the line of centers contributes to the dissociation. If it is assumed that the internal degrees of freedom of the colliding partners may also contribute to the dissociation energy, the equation for the rate constant becomes⁽¹⁰⁾

$$k = PZ \frac{(D/RT)^{n/2}}{(n/2)!} e^{-D/RT} \quad (6)$$

where n is the number of squared terms of momentum or coordinate contributing to the energy of the available internal degrees of freedom, and

P = collision efficiency

Z = collision frequency

D = dissociation energy.

Since Z is proportional to $T^{1/2}$, Equation (6) can be recast into the form

$$\log \frac{k_A}{T^{1/2}} + \frac{1}{2.303} \frac{D}{RT} = \log \frac{PZ}{T^{1/2}} - \log \left(\frac{n}{2}! \right) + \frac{n}{2} \log \frac{D}{RT} \quad (7)$$

A plot of the left side of Equation (7) against $\log D/RT$ should be a straight line with a slope of $n/2$ and an intercept of $\log (PZ/T^{1/2}) - \log (n/2!)$. A least-square fit of Equation (7) yields

$$k_A = 9.33 \times 10^9 T^{1/2} \frac{(126,000/RT)^{5.96}}{5.96!} e^{-126,000/RT} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1} \quad (8)$$

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This equation is plotted in Figure 3 as the slightly curved dotted line. The equation suggests a value of $n/2$ equal to about six, corresponding to about six classical oscillators or twelve squared energy terms. Carbon dioxide has four vibrational modes which provide eight squared terms and the two rotational modes each supply one squared term for a total of only ten. Thus, the observed temperature dependence can not be simply accounted for by the participation of the internal energy of carbon dioxide.

CARBON DIOXIDE-NITROGEN MIXTURES

The dissociation measurements in the nitrogen mixtures were carried out in the 3-inch shock tube. Because of the high heat capacity of the nitrogen diluent, it was necessary to work behind reflected shocks to produce the carbon dioxide dissociation temperatures. The dissociation was monitored at reflected shock temperatures from 3,100 to 7,700°K and pressures from 0.5 to 15 atm in mixtures of 0.25 to 20 percent carbon dioxide in nitrogen. Emission measurements were made 3 mm from the end wall to keep the times behind incident shocks low before arrival of the reflected shocks. It was found that the emission at 4.30μ in carbon dioxide-nitrogen mixtures decayed to a higher plateau than was obtained with the carbon dioxide-argon mixtures. Measurements made at 2.85μ on the long-wavelength edge of the 2.7μ atmospheric carbon dioxide absorption band were much better behaved. At 2.85μ , carbon monoxide interference is avoided. At elevated temperatures, the emission in the 2.7μ band moves to longer wavelengths and measurements at 2.85μ can be made without an enclosed optical system. Tourin⁽¹¹⁾ has shown that at 1,273°K the emissivity of carbon dioxide-nitrogen mixtures at 4.85μ is proportional to carbon dioxide concentrations and independent of total pressure over much of the range of optical densities and total pressures encountered in the current study. At the higher temperatures of this study, it can be expected that the emission at 2.85μ is proportional to the carbon dioxide concentrations as the dissociation proceeds. Hence, disappearance rates of carbon dioxide were determined for the carbon dioxide-nitrogen mixtures in the same manner as for the argon mixtures.

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The shock properties were calculated on the basis of the reaction occurring in vibrationally relaxed carbon dioxide and nitrogen. Over the range of conditions for the study, the vibrational relaxation time for nitrogen varies between 1 to 5 μsec ⁽¹²⁾ whereas the corresponding carbon dioxide decay times vary from 10 to 500 μsec . The carbon dioxide vibrational relaxation times are well below 1 μsec at the conditions of the study.⁽¹³⁾ Thus the assumption of vibrational relaxation prior to the occurrence of appreciable reaction appears to be a valid approximation.

Rate constants for the dilute mixtures (0.25 and 1.0 percent) of carbon dioxide in nitrogen are shown in Figure 4. For these dilute mixtures the assumption of constancy of temperature as the dissociation proceeds is most valid. A least-square fit of the Arrhenius equation to the data gives the overall bimolecular rate constant

$$k_{N_2} = 1.18 \times 10^{11} T^{1/2} e^{-73,200/RT} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1} \quad (9)$$

shown as the solid line in Figure 4. The probable error in the pre-exponential term is 50 percent, with a probable error of 3,500 cal/mol in the apparent activation energy. Using diameters of 3.75 Å for nitrogen and 4.59 Å for carbon dioxide gives a collision efficiency of about 0.01.

If internal modes are assumed to participate in the dissociation, a fit of Equation (6) to the data yields

$$k_{N_2} = 5.00 \times 10^9 T^{1/2} \frac{(126,000/RT)^{5.97}}{5.97!} e^{-126,000/RT} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1} \quad (10)$$

which is shown as the dotted curve in Figure 4. As with the argon mixtures, the equation indicates the participation of about six classical internal oscillators in the dissociation process along with the kinetic energy along the line of centers. For the carbon dioxide-nitrogen encounters, the possibility exists that the nitrogen might also contribute its internal energy to the dissociation coordinate. However, conservation of angular momentum prohibits the simultaneous participation of the rotational modes of nitrogen and carbon dioxide in the dissociation. If nitrogen contributes its vibrational energy to the dissociation

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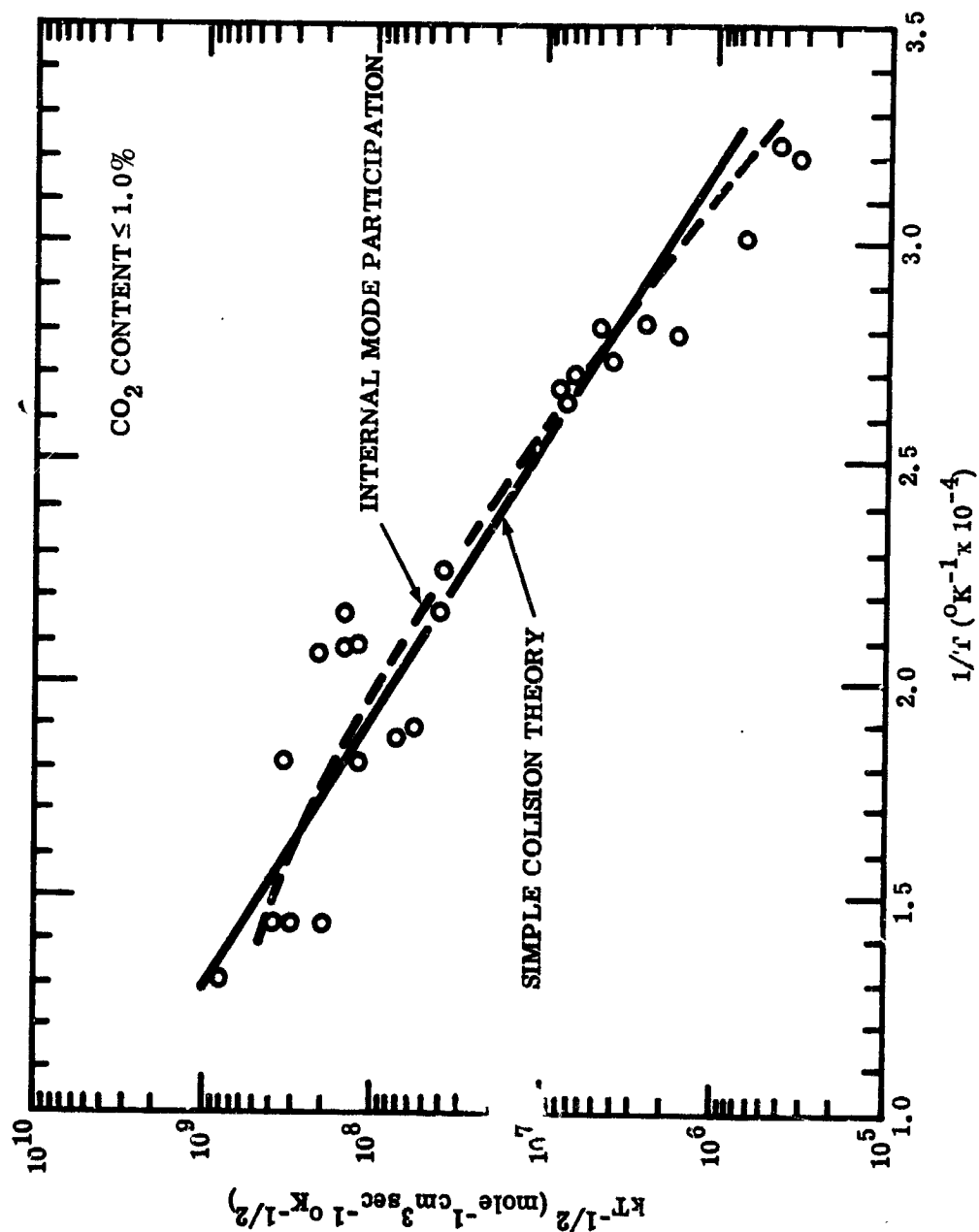


Figure 4 Bimolecular Rate Constants for Carbon Dioxide Dissociation in Nitrogen. CO₂ Content ≤ 1.0%

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process along with the internal energy of carbon dioxide, the total number of squared energy terms available in the encounter would be twelve. This would marginally satisfy the application of Equation (10) to the experimental data. However, the close similarity in the dissociation rate constants in the argon and nitrogen diluents suggest that the reaction goes by the same mechanism in both systems. Therefore, the participation of internal modes probably does not fully account for the observed temperature dependence of the dissociation rate.

Included in the data in Figure 4 are three tests on one percent mixtures of carbon dioxide in nitrogen at initial pressures of 1, 5, and 10 mm Hg, all brought to about the same temperature behind the reflected shocks. The results of these tests are listed in Table I.

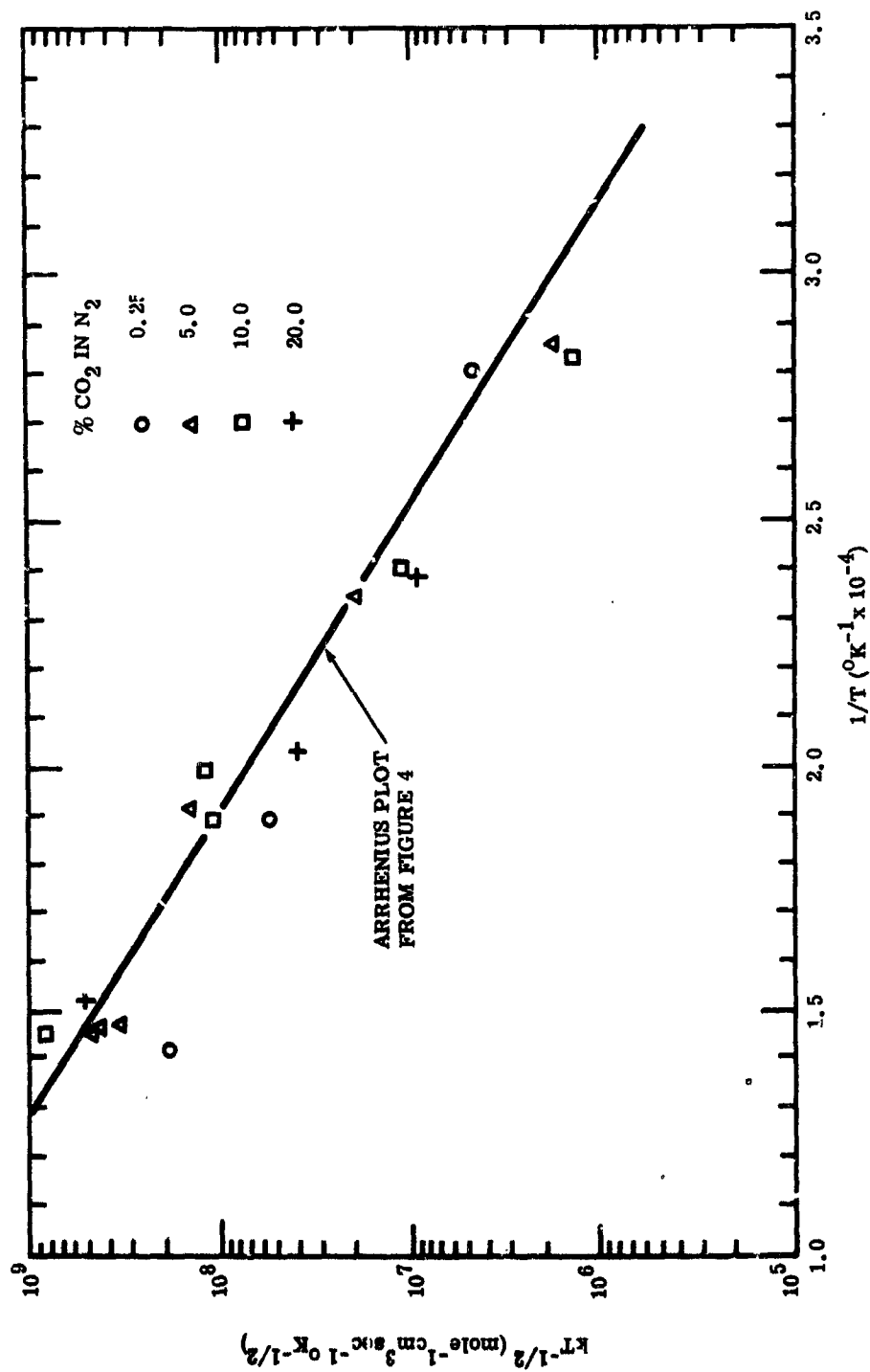
Table I
EFFECT OF TOTAL PRESSURE ON
DISSOCIATION RATE CONSTANT

Initial Pressure (mm Hg)	Shock Temp (°K)	Shock Pressure (atm)	k_{N_2} (mole ⁻¹ cm ³ sec ⁻¹)
1	4810	0.515	9.67×10^9
5	4880	2.79	1.53×10^{10}
10	4810	5.45	9.51×10^9

The rate constant for the series is relatively insensitive to the factor of ten variation in the total pressure and supports the assumption of the overall bimolecular process.

A series of tests were made on mixtures of up to 20 percent carbon dioxide in nitrogen. Although the assumption of an isothermal dissociation process is increasingly inaccurate as the carbon dioxide concentration increases, the rate constants determined under the simplifying assumptions were relatively insensitive to concentration and fell within the experimental uncertainty of the one-percent data. The data are compared with Equation (9) in Figure 5.

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Figure 5 Bimolecular Dissociation Constants for Mixtures of Varying CO_2/N_2

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The results of the present study are in reasonably close agreement with those of Davies,⁽⁵⁾ who gives

$$k_A = 2.45 \times 10^{11} T^{1/2} e^{-74,000/RT} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1} \quad (11)$$

and

$$k_{N_2} = 2.45 \times 10^{11} T^{1/2} e^{-74,500/RT} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1}. \quad (12)$$

The data of Brabbs, Bulles, and Zlatarich⁽⁴⁾ is given by

$$k_A = 3 \times 10^{11} T^{1/2} e^{-86,000/RT} \text{ mole}^{-1} \text{ cm}^3 \text{ sec}^{-1} \quad (13)$$

over the temperature range from 2,500 to 3,000°K. This data lies about an order of magnitude below the argon results of the present study.

Available carbon dioxide dissociation-rate data is summarized in Figure 6. A value calculated from some data of Hurle and Gaydon⁽³⁾ is also included. Their result was for pure carbon dioxide and would suggest that carbon dioxide is an order of magnitude more efficient than nitrogen or argon as a collision partner for the dissociation. All of the high temperature dissociation data has been obtained in shock tubes.

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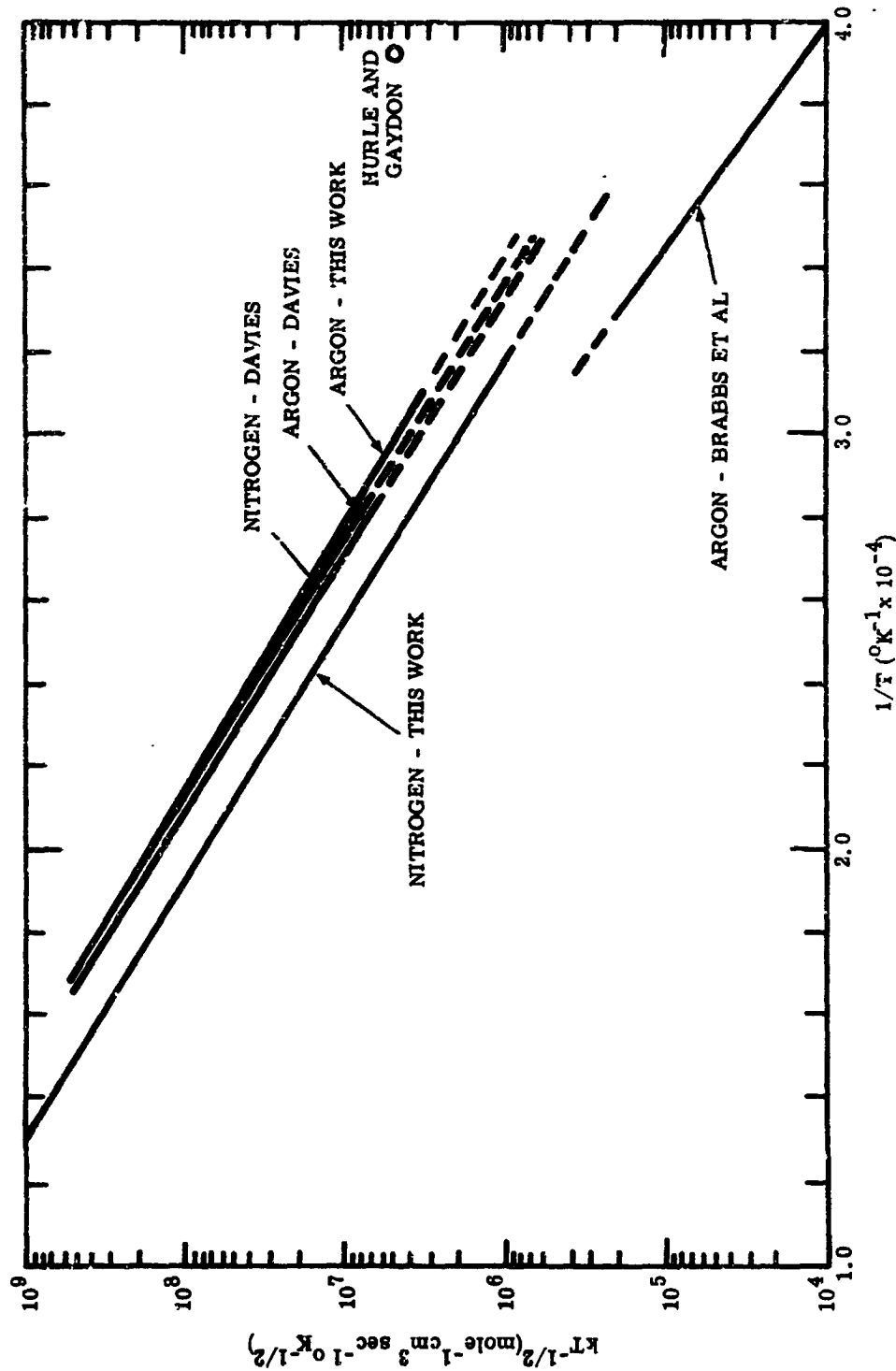


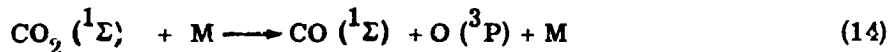
Figure 6 Summary of Carbon Dioxide Dissociation Results

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DISCUSSION

The dissociation rates of carbon dioxide in argon and nitrogen mixtures have been found to be very similar. Argon appears to be twice as efficient as nitrogen as a collision partner in the dissociation process. The bimolecular rate constants in dilute nitrogen mixtures were relatively insensitive to an order of magnitude variation in total pressure. Variation in carbon dioxide from 0.25 to 20 percent in nitrogen yielded results that were not significantly different. Although the accuracy of the data is not sufficient to assess the $\text{CO}_2\text{-CO}_2$ collision efficiency, it appears that carbon dioxide is not appreciably different from nitrogen.

The most interesting aspect of the dissociation is the apparent activation energy of 72–73 kcal/mol. This low value indicates that the dissociation does not go simply via



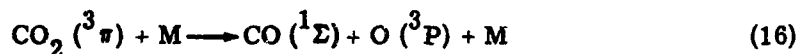
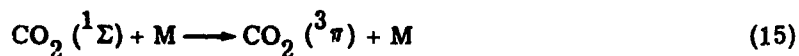
which requires 126 kcal/mol. In a number of studies it has been possible to reconcile an apparently low activation energy with a large dissociation energy through the participation of energy of internal modes in the dissociation act. Palmer and Hornig⁽¹⁴⁾ could account for the apparently low activation energy of the bromine dissociation through the participation of internal energy in the dissociation process. Similarly, Tsang, Bauer, and Cowperthwaite⁽¹⁵⁾ invoked the participation of internal energy in the shock dissociation of cyanogen. Similar treatment can not fully account for the argon mixtures in the present study, and at best is marginal for the nitrogen mixtures.

The apparently low temperature sensitivity may be a consequence of the coupling of the dissociation and vibrational relaxation processes. It has recently been demonstrated that the preferential dissociation from the higher vibrational levels

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of a molecule deplete these levels and effectively decrease the dissociation rate from the level that would exist if a Boltzmann distribution of vibrational states were to exist. Pritchard⁽¹⁶⁾ has carried out an analysis for hydrogen dissociation. With increasing temperature, the depletion of upper vibrational states becomes more severe and limits the rate of climb of the dissociation rate with temperature. Treanor and Marrone⁽¹⁷⁾ carried out a somewhat similar analysis for oxygen dissociation. The decrease in the apparent activation energy in going from Brabbs' study at 2,500 to 3,000°K to the present study from 3,300 to 6,000°K is consistent with the consequences of a vibrational-dissociation coupling of the kind described. Little work has been done with this model on other species. Brabbs, et al⁽⁴⁾ calculated rate constants based on a vibration-dissociation coupling model of Nikitin and Sokolov.⁽¹⁸⁾ The calculated rate constants were an order of magnitude greater than their data. Their calculated values are in close agreement with the results reported here for the argon mixtures. However, they calculated an activation energy of 112 kcal/mol, which is well above the 72 kcal/mol measured in the current study.

It has been suggested that the low activation energy may be a consequence of a two step dissociation process.⁽⁴⁾ The carbon dioxide is excited in a collision to a low lying electronic state from which the subsequent dissociation is rapid;



It has been estimated that the $\text{CO}_2 (^3\Pi)$ state lies between 55–95 kcal/mol above the ground state.⁽¹⁹⁾ Thus the 72–73 kcal/mol activation energy could be related to the excitation process of Equation (15). However, the direct excitation is spin forbidden. To avoid this obstacle, it has been proposed⁽⁴⁾ that the electronic excitation be achieved by a collision-induced transition from an excited vibrational level in the ground state, with little or no activation energy. Thus, the observed activation energy would populate a vibrational level of the ground state near the excited electronic state.

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Brabbs has also suggested that the singlet-triplet transition may be effected by collision of a vibrationally excited singlet carbon dioxide with triplet argon. This latter suggestion probably suffers from an insufficient supply of triplet argon to maintain the observed carbon dioxide dissociation rates, since the lowest lying argon triplet requires about 270 kcal/mol excitation. With nitrogen as a collision partner, the lowest lying triplet is about 144 kcal above the ground state and similar considerations are applicable.

The close agreement of the dissociation rates in nitrogen and argon suggest a common mechanism. Although it appears that the participation of internal degrees of freedom cannot fully account for the observed temperature dependencies, it is possible that this mechanism is partially operative. Hansen⁽²⁰⁾ has recently calculated rate constants for the dissociation of carbon dioxide based on the physically reasonable participation of three classical internal oscillator modes in the reaction. His calculated results for the carbon dioxide-argon system range from twice the experimental values at 3,600°K to about 10 times the experimental results at 5,900°K. It is possible that the observed temperature dependence is a consequence of the participation of internal energy in the reaction along with the depopulation of upper vibrational states. As temperature increases the latter effect would tend to increase the difference between the dissociation rates that would be obtained from an equilibrium distribution in the vibrational levels of the reacting molecule and the reaction-perturbed distribution. Quantitative assessment of the combined effects of internal energy participation and depletion of upper vibrational levels is indeed formidable.

Finally, a more complete assessment of the two-step process (Equations (15) and (16)) is required before it can be set aside. Detailed spectral measurements and studies of other collision partners might contribute to a better understanding of the mechanism of the high-temperature dissociation of carbon dioxide.

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